Fabrication of Thin Film Ceramic Membranes by Electrodeposition

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Thin films of yttria stabilized zirconia (YSZ), $Ce_{1-x}Gd_xO_y$ (CGO) and $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSGM) are of considerable importance for applications as electrolytes in solid oxide fuel cells (SOFC). A great deal of work has been done recently on development of advanced techniques for deposition of these materials. The formation of ceramic films by cathodic electrophoretic deposition (EPD) and electrolytic deposition (ELD) is especially attractive for the manufacturing of SOFCs. These methods offer important advantages such as low capital investment, rigid control of film thickness, uniformity of deposition rate as well as the possibility of formation of multilayer deposits of controlled thickness on substrates of complex shape. EPD requires the use of ceramic particles in suspension. Deposit uniformity and minimal deposit thickness are limited by the particle size. Owing to the use of ionic solutions instead of suspensions of ceramic particles, the deposits obtained via ELD have finer particle sizes and exhibit higher sintering activity. ELD allows formation of coatings from the atomic scale and is now an important tool in deposition of nanostructured thin films. However, the deposition rate of the EPD process is much faster. EPD and ELD as well as combined EPD/ELD methods can be applied for formation of advanced ceramic thin film materials.

In this paper experimental results are presented on ELD and EPD of YSZ, CGO and LSGM. Cathodic deposits were obtained at constant current densities ranging from 0.1 to 2 mA/cm^2 for EPD and from 2 to 10 mA/cm^2 for ELD. Ni foil and Ni-8YSZ cermets prepared by tape casting technology, were used as substrates. The deposition processes were quantified in experiments performed with Ni substrates, which were weighed before and after deposition followed by drying. ELD was performed from chloride and nitrate solutions. ELD processes were developed for formation of $Ce_{1-x}Gd_xO_y$ (x=0-0.2) and YSZ (Y/Z=0-0.22) films of thickness 0.1- 2 μm. By varying the Y/Zr and Gd/Ce atomic ratio in solutions and deposition time, the amount of the deposited material and its composition could be controlled. Deposit weight increased with time at constant current density as well as with current density at a constant deposition time. Nearly linear dependencies were observed. ELD deposits were obtained as monolayers or multilayers. The influence of current density, solvent composition and additives on deposit morphology has been studied. The deposits were characterized by X-ray diffraction, thermogravimetric analysis and scanning electron microscopy. The crystallization behavior of the deposits was also studied. X-ray analysis was made on as-formed deposits and those thermally treated in air at different temperatures. Fresh deposits contained a significant amount of amorphous phase. Deposit crystallization was observed after thermal dehydration of the amorphous precursors at 500°C. Thermogravimetric analysis revealed weight loss during heating, which is attributed to gradual decomposition of the precursors. Electrochemical intercalation of poly(diallyldimethylammonium chloride) into the deposits was demonstrated and the mechanism of intercalation is discussed. The experimental results indicate that the polymer acts as a binder, providing better adhesion of the organoceramic deposits and reducing cracking while allowing for film formation on porous substrates.

A suspension for EPD is a complex system in which each component has a substantial effect on deposition efficiency. Important factors to consider when selecting a binder-dispersant-solvent system are: chemical compatibility of components, solubility of binder and additives, viscosity and electric resistivity of the suspension. It was demonstrated that the ethyl alcohol - phosphate ester - polyvinyl butyral system is an effective solvent – dispersant - binder system for ELD of YSZ, CGO and LSGM. Problems, related to application of toxic materials, particle-additive interactions and corrosion of electrodes could be eliminated or diminished. Phosphate ester provides good dispersion and charging of ceramic particles. The phosphate ester is an effective electrostatic stabilizer, which charges the particles positively in ethyl alcohol solvent by donating protons to the surface. Moreover, phosphate ester acts as a steric dispersant by anchoring the long chain molecules to the particle surfaces. Prepared suspensions exhibited high stability and relatively high deposition rate can be achieved. Due to the use of an effective binder, obtained deposits adhered well to the substrates and exhibited enhanced stability against cracking. The influence of dispersant, binder and current density on deposition efficiency and deposit morphology was studied. The deposition rate was determined under constant current density and constant voltage regimes. The proposed solvent – dispersant - binder medium for electrophoretic deposition of LSGM, YSZ and CGO has important advantages and implications in fuel cell design. Cationic polyelectrolytes with inherent binding properties were also studied for charging and electrophoretic deposition of LSGM, YSZ and CGO. The efficiency of various polyelectrolytes was evaluated Deposition rate was studied at various experimental conditions. The deposition rate in the EPD process was much faster (by 1-2 orders of magnitude) than that in ELD process, resulting in significantly higher deposit thickness. The microstructure of the deposits was examined by electron microscopy. Electron microscopic investigations have shown that the microstructures of deposits were influenced by powder characteristics. The minimal thickness of EPD deposits (~1 micron) is determined by the size of particles used for deposition.

Our results indicate that films of LSGM, YSZ and CGO could be obtained via ELD and EPD for use in SOFC applications.